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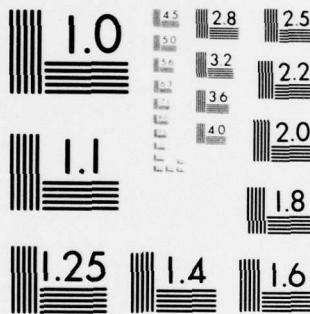
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Ionic Reactions Deduced From Atmosphere Explorer Data: A Survey.

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WILLIAM SWIDER

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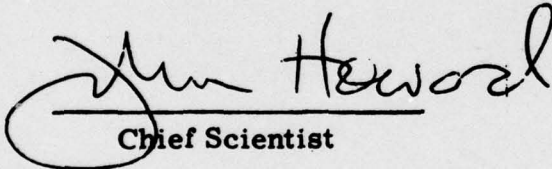


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Ionic Reactions Deduced From Atmosphere Explorer Data: A Survey

1. INTRODUCTION

The Atmosphere Explorer satellites were designed to make measurements of the atmosphere, principally the 150-400 km region, in order to determine better the photochemistry of this region. Three satellites belong to the AE series and they are commonly called AE-C, AE-D and AE-E. All three vehicles had (have) weights of 700 ± 50 kg. They were launched into low perigee high eccentricity orbits with different inclinations. A propulsion system was used to maintain an elliptical orbit for about 1 year. AE-C and AE-E were put into circular orbits near 250 km following their elliptical orbit phase. The first in the series, AE-C was launched into a 68° inclination orbit on 13 December 1973. More than 25,000 orbits of data have been obtained with this satellite. The second vehicle, launched into a polar orbit (90° inclination) on 6 October 1975 had an abbreviated life as a result of a failure somewhere in the power system. The useful life ended on 29 January 1976 with approximately 1400 orbits of data. The final spacecraft, AE-E, is still operational. In fact, there are plans to place AE-E in as high an orbit as possible in order to continue EUV measurements for as long as feasible. The only member of the series to be launched from Cape Canaveral (on 20 November 1975), the orbital inclination is about 20° for this satellite.

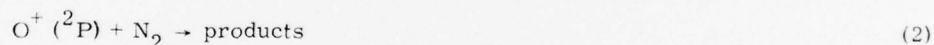
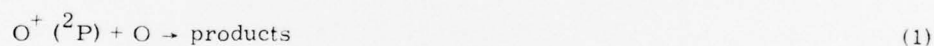
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A variety of experiments under 15, 14 and 13 principal investigators, respectively, for AE-C, AE-D and AE-E were flown aboard these spacecrafts, most experiments being on all three vehicles. Measurements were taken of electron concentration and temperature, ion temperature, total density, neutral and ion composition, photoelectron flux (0-500 eV), energetic electrons (0.2-25 keV), nitric oxide gamma bands, solar EUV (170-1700Å), selected airglow emissions and various spacecraft operational information. Further details are available in the April 1973 issue of Radio Science which is devoted to a description of the overall program. The "1975 Report on Active and Planned Spacecraft and Experiments" NSSDC/WDC-A-R&S, 75-01, also may be consulted.

This report summarizes results deduced by the various experimentalists and "guest" investigators from the many orbits of data collected by AE-C, D and E. We restrict ourselves to an assessment of the ion chemistry results announced in 23 published papers, most relating to AE-C data. A 24th paper is cited also which was stimulated by, but does not involve the data directly. In the course of writing this survey, a review of the same subject matter considered here was published.¹ That (25th) paper should be read also by the interested reader and compared with the survey here which is taken from a somewhat different perspective.

2. METASTABLE ATOMIC OXYGEN IONS

Dayglow radiation at 7319Å which was obtained on orbit 459 of AE-C on 27 January 1974 (the satellite being despun on this pass) was used by Walker et al² to estimate quenching rates of $O^+ (^2P)$ with O and N_2

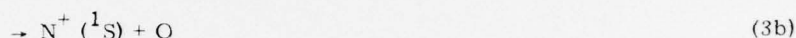
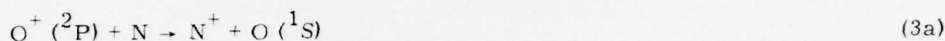


assuming that the theoretical quenching rate for this metastable ion with electrons is as published. (No effort was placed into defining the reaction products.) They determined rate coefficients, k , for the quenching of $O^+ (^2P)$ with atomic oxygen and molecular nitrogen of $2 \times 10^{-10} \text{ cm}^3/\text{sec}$ (k_1) and $5 \times 10^{-11} \text{ cm}^3/\text{sec}$ (k_2), respectively. However, they noted that similar results are reached if a rate

1. Torr, D.G., and Torr, M.R. (1978) Review of rate coefficients of ionic reactions determined from measurements made by Atmosphere Explorer Satellites, Rev. Geophys. Space Phys. 16(3):327-340.
2. Walker, J.C.G., Torr, D.G., Hays, P.B., Rusch, D.W., Docken, K., Victor, G., and Oppenheimer, M. (1975) Metastable 2P oxygen ions in the daytime thermosphere, J. Geophys. Res. 80(7):1026-1029.

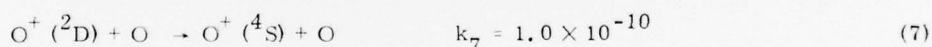
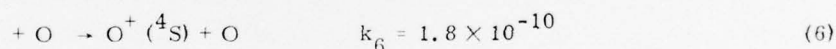
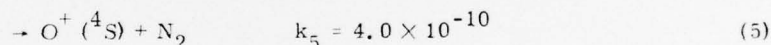
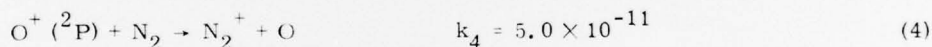
coefficient $k_2 = 5 \times 10^{-10} \text{ cm}^3/\text{sec}$ is adopted with no quenching by atomic oxygen, $k_1 = 0$. In a more recent paper Rusch et al.³ determined values of $(5.2 \pm 2.5) \times 10^{-11} \text{ cm}^3/\text{sec}$ for k_1 and $(4.8 \pm 1.4) \times 10^{-10} \text{ cm}^3/\text{sec}$ for k_2 from an analysis of AE-C and D data on the OII ($^2\text{P} - ^2\text{D}$) transition at 7319 and 7330 Å.

The metastable ion, $\text{O}^+ (^2\text{P})$ can resonantly charge exchange with atomic nitrogen according to Torr et al.,⁴ leaving the atomic oxygen product in a ^1S state (ultimately),



and thereby providing a significant source of $\text{O} (^1\text{S})$ in the auroral F-region, since $\text{N}^+ (^1\text{S}) + \text{O} \rightarrow \text{N}^+ + \text{O} (^1\text{S})$ is nearly resonant also. They give $k_3 = 1.7 \times 10^{-9} \text{ cm}^3/\text{sec}$. (The latter species decays to the ^1D state while emitting a 5577 Å photon.) This conclusion was based upon an analysis of AE-C data on 14 July 1974 taken just after midnight in an aurora at F-region altitudes. It should be noted that they also found good agreement between their ion model and the measured ions O_2^+ , NO^+ and N_2^+ using the conventional laboratory results then available.

Oppenheimer et al.⁵ estimated the following rate coefficients for metastable O^+ ions using AE-C observations:

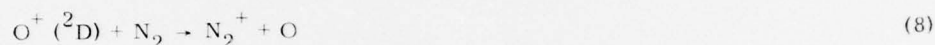


However, they did emphasize that these derived absolute rate constants may not be unique. The rate constants $k_4 + k_5$ and k_6 may be compared with the rate

3. Rusch, D.W., Torr, D.G., Hays, P.B., and Walker, J.C.G. (1977) The OII (7319-7330 Å) dayglow, *J. Geophys. Res.* 82(4):719-726.
4. Torr, M.R., Hoffman, R.A., Hanson, W.B., Hoffman, J.H., Torr, D.G., Peterson, W.K., and Walker, J.C.G. (1975) An auroral F-region study using in situ measurements by the Atmosphere Explorer-C Satellite, *Planet. Space Sci.* 23(12):1669-1679.
5. Oppenheimer, M., Dalgarno, A., and Brinton, H.C. (1976) Ion chemistry of N_2^+ and the solar ultraviolet flux in the thermosphere, *J. Geophys. Res.* 81(22):3762-3766.

coefficients k_1 and k_2 . Since the latter two coefficients refer to only quenching, the relationships $k_1 \geq k_6$ and $k_2 \geq k_4 + k_5$ should hold and, in fact, do hold. However, neither set is necessarily unique as indicated by two^{2, 5} of the three groups of authors.

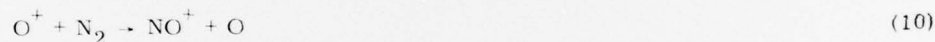
Orsini et al,⁶ using a much more extensive data base than earlier studies had available, lowered an earlier estimate of the rate coefficient k_7 . Their upper limit is now 3×10^{-11} cm³/sec, that is, $k_7 < 3 \times 10^{-11}$ cm³/sec, for this process. Torr et al⁷ determined a rate coefficient, k_8 of $5 \pm 2.5 \times 10^{-10}$ cm³/sec for



from AE-C observations.

3. GROUND STATE ATOMIC OXYGEN IONS

Rate coefficients inferred from the analysis of AE data are compatible with laboratory rate coefficients for the same reactions:

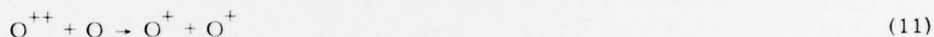


Oppenheimer et al⁸ and Torr et al⁹ found that the laboratory rate constant, k_9 , 2×10^{-11} (300/T)^{0.4} for process (9) is consistent with both AE observations and most other laboratory results. However, Oppenheimer et al⁸ noted that the scatter of the AE data is such that a rate coefficient 30 percent smaller at 900° K is not unreasonable. In a subsequent assessment, Oppenheimer et al¹⁰ used the

6. Orsini, N., Torr, D.G., Torr, M.R., Brinton, H.C., Brace, L.H., Nier, A.O., and Walker, J.C.G. (1977) Quenching of metastable ²D oxygen ions in the thermosphere by atomic oxygen, J. Geophys. Res. 82(29):4829-4833.
7. Torr, D.G., and Orsini, N. (1977) Charge exchange of metastable ²D oxygen ions with N₂ in the thermosphere, Planet. Space Sci. 25(12):1171-1176.
8. Oppenheimer, M., Dalgarno, A., and Brinton, H.C. (1976) Molecular oxygen abundances in the thermosphere from Atmosphere Explorer-C ion composition measurements, J. Geophys. Res. 81(25):4678-4684.
9. Torr, D.G., Torr, M.R., Walker, J.C.G., Nier, A.O., Brace, L.H., and Brinton, H.C. (1976) Recombination of O₂⁺ in the ionosphere, J. Geophys. Res. 81(31):5578-5580.
10. Oppenheimer, M., Constantinides, E.R., Kirby-Docken, K., Victor, G.A., and Dalgarno, A. (1977) Ion photochemistry of the thermosphere from Atmosphere Explorer-C measurements, J. Geophys. Res. 82(35):5485-5492.

laboratory rate coefficient, k_9 , without comment, in reaching good agreement between their ion chemistry model and the AE data. Torr et al¹¹ ascertained a rate coefficient, k_{10} , of $1.2 \times 10^{-12} (T_i/300)^{-0.8} \text{ cm}^3/\text{sec}$ for process (10) over a temperature range of 500-1200°K. This result was based upon over 5300 simultaneous ion and neutral concentration and temperature points as recorded by AE-C. This value is in excellent agreement with the laboratory data of the NOAA Boulder group. Oppenheimer et al¹⁰ employed a temperature independent rate coefficient, $k_{10} = 6 \times 10^{-13} \text{ cm}^3/\text{sec}$ for reaction (10) because the previously cited AE and laboratory work suggest only a very slow variation of this rate coefficient with temperature between 600 and 1000°K.

Some doubly charged atomic oxygen ions are produced in the daytime thermosphere. Breig et al¹² found that the major loss process is

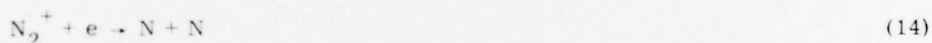
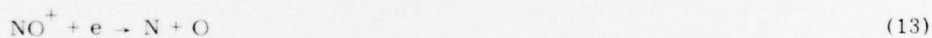
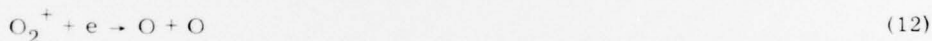


with a rate coefficient, k_{11} , of $1 \times 10^{-11} \text{ cm}^3/\text{sec}$.

4. DISSOCIATIVE RECOMBINATION REACTIONS

The principal molecular ions of the F-region are NO^+ and O_2^+ ions. However, there also is interest in N_2^+ ions because they are the major initial ions in the low F-region and their chemistry is pertinent to N and NO and hence NO^+ ions.

Torr et al⁴ applied dissociative recombination rates for



as measured by the Pittsburgh group and found them suitable for AE-C F-region auroral data analysis. However, Torr et al¹³ later determined that the dissociative

11. Torr, M.R., St.-Maurice, J.P., and Torr, D.G. (1977) The rate coefficient for the $\text{O}^+ + \text{N}_2$ reaction in the ionosphere, J. Geophys. Res. 82(22): 3287-3290.
12. Breig, E.L., Torr, M.R., Torr, D.G., Hanson, W.B., Hoffman, J.H., Walker, J.C.G., and Nier, A.O. (1977) Doubly charged atomic oxygen ions in the thermosphere 1, Photochemistry, J. Geophys. Res. 82(7):1008-1012.
13. Torr, D.G., Torr, M.R., Walker, J.C.G., Brace, L.H., Brinton, H.C., Hanson, W.B., Hoffman, J.H., Nier, A.O., and Oppenheimer, M. (1976) Recombination of NO^+ in the ionosphere, Geophys. Res. Lett. 3(4):209-212.

recombination rate for NO^+ ions more closely followed results published by a group at JILA. Oppenheimer et al¹⁴ reached the same conclusion. Torr et al⁹ also have asserted that the dissociative recombination rate for O_2^+ ions best fits the JILA laboratory results of this same pair of experimentalists.

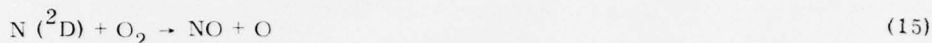
There has been considerable controversy over the dissociative recombination rate for N_2^+ ions. Orsini et al¹⁵ claimed that their interpretation of AE data led to a slight increase of this rate coefficient with temperature which behavior they suggested may be a consequence of high N_2^+ vibrational excitation. (I am not aware of any dissociative recombination rate which increases with temperature over the range 300-3000°K.) Biondi,¹⁶ in fact, has objected to the conclusions of Orsini et al,¹⁵ and he has suggested that perhaps an increase in the rate coefficient of $\text{N}_2^+ + \text{O} \rightarrow \text{N} + \text{NO}^+$ as a result of vibrationally excited N_2^+ might alter the results of Orsini et al.¹⁵ Torr and Orsini¹⁷ have countered with the suggestion that the dissociative recombination rate for N_2^+ ions as determined from AE data can be reconciled with the laboratory measurements if the charge exchange rate between $\text{O}^+ (^2\text{D})$ and N_2 process (8), is less than 1/4 of the laboratory derived rate coefficient. This suggestion seems quite reasonable since the laboratory results only went down to 0.5 eV in the laboratory system. A more detailed thermal energy study appears to be warranted. Furthermore, Torr et al¹⁸ found the process $\text{N}_2^+ + \text{O} \rightarrow \text{NO}^+ + \text{N}$ to be in excellent agreement with the NOAA Boulder Laboratory results.

5. NITROGEN REACTIONS

Although it is a minor constituent of the F-region, atomic nitrogen plays an important role in F-region chemistry, especially if its lowest metastable state

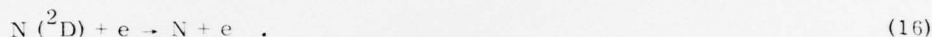
14. Oppenheimer, M., Dalgarno, A., Trebino, F.B., Brace, L.H., Brinton, H.C., and Hoffman, J.H. (1977) Daytime chemistry of NO^+ from Atmosphere Explorer-C measurements, *J. Geophys. Res.* 82(1):191-194.
15. Orsini, N., Torr, D.G., Brinton, H.C., Brace, L.H., Hanson, W.B., Hoffman, J.H., and Nier, A.O. (1977) Determination of the N_2^+ recombination rate coefficient in the ionosphere, *Geophys. Res. Lett.* 4(10): 431-433.
16. Biondi, M.A. (1978) Objections to the $\text{N}_2^+ + e^-$ dissociative recombination coefficients inferred from analysis of Atmosphere Explorer measurements, *Geophys. Res. Lett.* 5(8):661-664.
17. Torr, D.G., and Orsini, N. (1978) The effect of N_2^+ recombination on the aeronomic determination of the charge exchange rate coefficient of $\text{O}^+ (^2\text{D})$ with N_2 , *Geophys. Res. Lett.* 5(8):657-659.
18. Torr, D.G., Orsini, N., Torr, M.R., Hanson, W.B., Hoffman, J.H., and Walker, J.C.G. (1977) Determination of the rate coefficient for the $\text{N}_2^+ + \text{O}$ reaction in the ionosphere, *J. Geophys. Res.* 82(10):1631-1634.

(^2D) is considered. Rusch et al¹⁹ concluded that N (^2D) production from $\text{N}_2^+ + \text{e}$, process (14), exceeded that from $\text{NO}^+ + \text{e}$, $\text{N}_2^+ + \text{O}$, $\text{e} + \text{N}_2$ and $\text{N}^+ + \text{O}_2$. They found the rate coefficient for



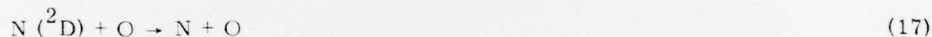
to be in the range $0 - 2.7 \times 10^{-12} \text{ cm}^3/\text{sec}$, somewhat lower than the laboratory measurements, but Frederick and Rusch²⁰ later concluded that AE-C and AE-D analyses agreed with the laboratory results for this process.

Rusch et al¹⁹ estimated a rate coefficient of about $1 \times 10^{-9} (\text{Te}/300)^{1/2}$ for the quenching of N (^2D) by electrons



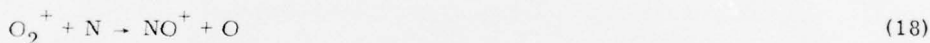
Their k_{16} is about twice an old theoretical value of which they were apparently unaware, since it is not quoted in their paper. Frederick and Rusch²⁰ reached a value for k_{16} in harmony with the theoretical value.

Torr et al²¹ used the higher k_{16} value of Rusch et al¹⁹ in their analysis of the quenching of N (^2D) by atomic oxygen,



for which they report $k_{17} = 1.5 - 2.5 \times 10^{-12} \text{ cm}^3/\text{sec}$. This determination is compatible with the laboratory rate constant for this process which they quote and with an efficiency²¹ of $(0.8 - 1.0) \pm 30$ percent for the production of N (^2D) by the dissociative recombination of NO^+ ions. Frederick and Rusch²⁰ ascertained that the quenching rate k_{17} is $4 \times 10^{-13} \text{ cm}^3/\text{sec}$, smaller than the laboratory result by about a factor of 5.

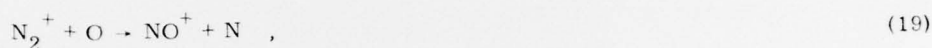
The NOAA Boulder Laboratory determined a rate coefficient for



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19. Rusch, D.W., Stewart, A.I., Hays, P.B., and Hoffman, J.H. (1975) The N I (5200Å) dayglow, J. Geophys. Res. 80(16):2300-2304.
 20. Frederick, J.E., and Rusch, D.W. (1977) On the chemistry of metastable atomic nitrogen in the F region deduced from simultaneous satellite measurements of the 5200Å airglow and atmospheric composition, J. Geophys. Res. 82(25):3509-3517.
 21. Torr, M.R., Burnside, R.G., Hays, P.B., Stewart, A.I., Torr, D.G., Walker, J.C.G. (1976) Metastable ^2D atomic nitrogen in the mid-latitude nocturnal ionosphere, J. Geophys. Res. 81(4):531-537.

of $1.8 \times 10^{-10} \text{ cm}^3/\text{sec}$, but an AE-C study by Torr et al²² suggested that k_{18} could be as low as $1 \times 10^{-10} \text{ cm}^3/\text{sec}$. Again, this result is not dramatic since absolute accuracies for these two values must overlap. For product O in the ^1S state, Frederick et al²³ found a rate coefficient of $2.5 \times 10^{-11} \text{ cm}^3/\text{sec}$ would explain the visible airglow experiment (VAE) on AE-C in regards to the observed 5577Å line emission. (This implies 15-25 percent of product O for process (18) is in the ^1S state, depending upon which total k_{18} value is accepted.) This VAE work was further amplified by Kopp et al.²⁴

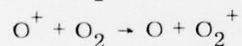
Finally, in regards to the important process



Torr et al¹⁸ deduced a rate coefficient from AE-C data which is consonant with the NOAA Boulder Laboratory result for this reaction.

6. F-REGION PROCESSES OF INTEREST TO DNA

Six reactions are of particular interest to DNA:



The AE data base has shed no information on the first two processes which are of little importance to the non-nuclear disturbed F-region. There has been no information forthcoming on the next two reactions either. However, there is a laboratory derived rate constant for $\text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O}$ and a Harvard University group,

22. Torr, D.G., Torr, M.R., Rusch, D.W., Hays, P.B., Mauersberger, K., Walker, J.C.G., Spencer, N.W., Hedin, A.E., Brinton, H.C., and Theis, R.F. (1976) Atomic nitrogen densities in the thermosphere, Geophys. Res. Lett. 3(1):1-4.
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under a contract supported by the DNA work unit cited for this report, is assessing AE data for the purpose of deriving a rate constant for the process $N^+ + O \rightarrow N + O^+$.

As regards the final two reactions, we have noted that AE results support the laboratory determinations, which unfortunately do not attain as high a temperature as desired. DNA requires these processes up to as high as 4000°K , but the AE satellites were in orbit during relatively low solar activity and even for high solar activity the maximum exospheric temperature is about 2000°K . Perhaps an assessment of AE data under very disturbed auroral conditions would be of value, since temperatures, and particularly $N_2(v)$ temperatures, might be somewhat higher under such conditions. It should be noted, however, that in regard to these two processes St.-Maurice and Torr²⁵ have derived from theoretical considerations and laboratory data, rate constants for "effective" temperatures up to about 6000°K which may be of value to the DNA community. Their deductions, although not derived from AE data, were certainly stimulated by their related investigations of the data.

7. SUMMARY AND CONCLUSIONS

F-region reaction rates derived from the Atmosphere Explorer series of satellites have agreed well with laboratory determined rate constants for the same processes with few exceptions. This agreement has been an important step in validating laboratory rate coefficients for atmospheric modelling work. (The ionic rate coefficients surveyed here are listed in the Appendix with comments.) Rate coefficients for a few reactions involving metastable ions have been derived which are not available from laboratory work. Few additional insights have been gained with respect to the six F-region processes of particular interest to the DNA community. However, some information of value may still be forthcoming.

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Appendix A

Summary of Ionic Rate Coefficients Deduced From the Atmosphere Explorer Satellites

IONIC REACTIONS

| Ref. | Equation No. in Text | Reaction | Rate Coefficient (cm ³ /sec) | Comment |
|--------|----------------------------|---|---|--|
| 3 | (1) | $O^+(^2P) + O \rightarrow \text{products}$ | $(5.2 \pm 2.5) \times 10^{-11}$ | See specific products below |
| 3 | (2) | $+ N_2 \rightarrow \text{products}$ | $(4.8 \pm 1.4) \times 10^{-10}$ | |
| 4 | (3a) (3b) | $O^+(^2P) + N \rightarrow N^+ + O(^1S) \}$ $\quad \quad \quad \rightarrow N^+(^1S) + O \}$ | 1.7×10^{-9} | |
| 5 | (4) | $O^+(^2P) + N_2 \rightarrow N_2^+ + O$ | 5.0×10^{-11} | |
| 5 | (5) | $\quad \quad \quad \rightarrow O^+ + N_2$ | 4.0×10^{-10} | |
| 5 | (6) | $O^+(^2P) + O \rightarrow O^+ + O$ | 1.8×10^{-10} | |
| 7 | (8) | $O^+(^2D) + N_2 \rightarrow N_2^+ + O$ | $(5 \pm 2.5) \times 10^{-10}$ | |
| 6 | (7) | $O^+(^2D) + O \rightarrow O^+ + O$ | $< 3 \times 10^{-11}$ | |
| 8, 9 | (9) | $O^+ + O_2 \rightarrow O_2^+ + O$ | $2 \times 10^{-11} \left(\frac{300}{T_i} \right)^{0.4}$ | as in labora- tory, but see also ref. 25 |
| 10, 11 | (10) | $O^+ + N_2 \rightarrow NO^+ + O$ | $1.2 \times 10^{-12} \left(\frac{300}{T_i} \right)^{0.8}$ $T < 1500^\circ K.$ | as in labora- tory, but see also ref. 25 |
| 12 | (11) | $O^{++} + O \rightarrow O^+ + O^+$ | 1×10^{-11} | |

IONIC REACTIONS (Cont.)

| Ref. | Equation No. in Text | Reaction | Rate Coefficient (cm ³ /sec) | Comment |
|---------------|----------------------------|---|--|--|
| 18 | (19) | $\begin{aligned} \text{N}_2^+ + \text{O} &\rightarrow \text{NO}^+ + \text{N}(^2\text{D}) \\ &\rightarrow \text{O}^+ + \text{N}_2 \end{aligned}$ | $\left. \begin{aligned} 1.4 \times 10^{-10} \\ \times \left(\frac{T_i}{300} \right)^{-0.44} \end{aligned} \right\}$ | as in laboratory |
| 22 | (18) | $\text{O}_2^+ + \text{N} \rightarrow \text{NO}^+ + \text{O}$ | 1×10^{-10} | laboratory result is 1.8×10^{-10} |
| 9 | (12) | $\text{O}_2^+ + e \rightarrow \text{O} + \text{O}$ | $\left. \begin{aligned} 1.6 \times 10^{-7} \\ \times \left(\frac{T_e}{300} \right)^{-0.65} \end{aligned} \right\}$ | as in JILA laboratory |
| 13, 14 | (13) | $\text{NO}^+ + e \rightarrow \text{N} + \text{O}$ | $\left. \begin{aligned} 4.2 \times 10^{-7} \\ \times \left(\frac{T_e}{300} \right)^{-0.85} \end{aligned} \right\}$ | |
| 15, 16, 17 | (14) | $\text{N}_2^+ + e \rightarrow \text{N} + \text{N}$ | $\left. \begin{aligned} 1.8 \times 10^{-7} \\ \times \left(\frac{T_e}{300} \right)^{-0.5} \end{aligned} \right\}$ | as in Pitts- burgh Labora- tory |

Note: All states are ground states generally, unless shown otherwise; exceptions are the dissociative recombination processes where an important fraction of the neutral products are in excited states. See Section 5 of text for comments on neutral reactions involving N(²D).

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